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INFLUENCE OF CADMIUM ADDITIVES ON THE RATE OF THERMAL AND RADIOCHEMICAL DECOMPOSITION OF SILVER CARBONATE

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ABSTRACT

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The addition of cadmium carbonate (2.5 mol. %) and its effect on the thermal decomposition of silver carbonate at 151°C, the radiochemical sensitization of the thermal decomposition process by prior x-irradiation, and the radiation decomposition of the carbonate under the influence of x-rays has been investigated. It has been established that the addition of 2.5 mol. % cadmium carbonate impurity to silver carbonate increases the rate of thermal and radiochemical decomposition of the silver carbonate. The hypothesis is advanced that the observed increase in the process rate may be attributed to an increase in the defect state of the silver carbonate crystals during addition of the impurity.

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In the literature, we find data pertaining to the effects on the thermal decomposition of solids due to impurities incorporated in their lattice during preparation (refs. 1-8). It would not be reasonable, however, to consider the indicated problem as having been exhaustively studied. Specifically, experimental data are lacking in which the influence of impurities on the thermal decomposition of compounds has been treated from the point of view of processes involving severance of the chemical bond within the anionic or cationic components of the lattice. The object of the present paper is to elucidate the

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*Numbers in the margin indicate pagination in the original foreign text.

effect of cadmium ion impurities on the thermal decomposition of silver carbonate which has been previously subjected to radiochemical sensitization of its thermal decomposition process and radiolysis by treatment with x-rays.

The silver carbonate (sample 1) was prepared by pouring together 0.05 N solutions of silver nitrate and sodium carbonate. The resultant precipitate was washed with water eight to ten times, subsequently dried over concentrated sulfuric acid and P_2O_5, and stored in an exsiccator. The preparation of mixed silver and cadmium carbonates (sample 2) was obtained by a similar procedure with a 0.05 N solution of silver nitrate containing 2.5 mol. % $CdNO_3$. All of the operations for deriving and drying the preparations, as well as their storage and sampling were carried out under conditions of photographic darkness. The similar values of the solubility products of the silver and cadmium carbonates indicated that the composition of the coprecipitated silver and cadmium carbonates (sample 2) corresponded to 97.5 mol. % AG_2CO_3 + 2.5 mol. % $CdCO_3$.

The similar values of the ionic radii of Ag^+ and Cd^{++}, on the other hand (according to Goldschmidt, r_{Ag} = 1.13 A; r_{Cd} = 1.03 A), attests to the actual possibility of obtaining solid solutions of silver and cadmium carbonates. Debye patterns which we recorded in order to verify this assumption indicated that when silver carbonate is coprecipitated with cadmium carbonate, there is an increase in the spacings between lattice planes, thus evincing the formation of solid solutions.

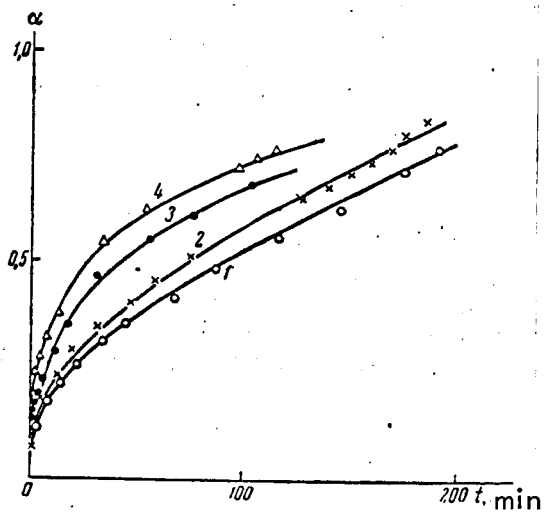
The investigation of the thermal decomposition kinetics was conducted at 151°C by gravimetric analysis, using a spring-loaded quartz balance; the coil of the balance made it possible to record weight fluctuations correct to $4 \cdot 10^{-5}$ g. The reaction volume was thermostatically controlled correct to within

±0.2°C. The evolved gaseous reaction products were continuously pumped off. For the experiments, we used particles with a dispersity of (8 to 14)$\cdot 10^{-3}$ cm.

For the preliminary irradiation we used x-rays from a type RUP-2 x-ray machine with a 1 BPM-200 tube (operating conditions: U_a = 200 kV, I_a = 20 mA).

The rate of radiation decomposition was estimated from the variation in whiteness of the test samples, using a model FM-1 general-purpose photometer. /366

The kinetic analysis of the data so obtained was performed on the basis of the equation $1 - \alpha = e^{-kt^n}$, where α is the fraction of completely reacting substance, t is the time in minutes (ref. 9), and the rate constant was computed according to the relation $K = nk^{1/n}$ (ref. 10).



Influence of the Addition of Cadmium Carbonate on the Rate of Thermal Decomposition of Silver Carbonate:

Sample 1: 1) nonirradiated; 2) radiation dose of 60 000 R; Sample 2: 3) nonirradiated; 4) radiation dose of 60 000 R.

The results of the experiments are shown in the figure. Table 1 summarizes the results of the kinetic analysis of the experimental data. It is apparent from the figure and from the table that the coprecipitation of silver carbonate with cadmium carbonate, with the latter in the amount of 2.5 mol. %, leads to

a sizable increase in the rate of thermal decomposition of silver carbonate.

The figure presents data on the influence of preliminary x-irradiation on the thermal decomposition of the carbonates. The data shown there exhibit an increase in the rate of thermal decomposition of silver carbonate after preliminary irradiation.

TABLE 1

KINETIC PARAMETERS OF THE DECOMPOSITION OF PURE SILVER CARBONATE AND WITH THE ADDITION OF CADMIUM CARBONATE

Sample	$K \cdot 10^4$ min^{-1}	n
1	4.5	0.505
1	4.9	0.515
2	11.6	0.477
2	12	0.469
1	6.95	0.515
2	13.6	0.45

TABLE 2

EFFECT OF X-IRRADIATION ON PURE SILVER CARBONATE AND WITH THE ADDITION OF CADMIUM CARBONATE

Dose, R	Filter	Optical reflectivity			
		Sample 1		Sample 2	
0	Red	39	38	42	40
	Green	37		40	
	Blue	38		38	
30 000	Red	32	32	29	30
	Green	31		31	
	Blue	32		29	
45 000	Blue	27		22	

Data relating to the influence of x-rays on samples 1 and 2 are given in Table 2. As evident from the table, the rate of radiation decomposition of silver carbonate increases with the addition of cadmium carbonate impurity (sample 2).

In reference 11, which is devoted to an investigation of the possible ways in which defects in crystals could affect the thermal decomposition of solids, a certain advantage is indicated in treating this influence as a function of the characteristics of the decomposition reaction mechanism. It is a well known fact that the decomposition of carbonates in general, silver carbonate in particular, takes place with a severance of the bond inside the anion (ref. 12). An x-ray analysis that we performed on the solid reaction products showed that the product of decomposition is silver oxide. Consequently, in the spirit of the postulates developed in reference 11, the presence of Cd^{++} ions in the /367 silver carbonate lattice must lead to distortions and deformation of the silver carbonate lattice, thus accelerating its thermal decomposition. If the decomposition of the solid takes place with severance of the bond between the anion and cation, then in appraising the influence of impurities on its thermal decomposition, not only must the acceleration of decomposition due to deformation of the crystal lattice by the impurity be taken into account, in influence of the impurity on the electronic and ionic processes responsible for thermal decomposition must be considered as well (refs. 13 to 15). Allowance for the latter if of vital importance. As we showed in the example of silver oxylate (ref. 3), the contribution of the impurity to electronic processes in thermal decomposition may be attributed to a deceleration of decomposition of the oxylate with the incorporation of cadmium ions in its lattice, the opposite effect of that which we observed in the example of Ag_2CO_3. The acceleration of the radiation decomposition of silver carbonate by a cadmium impurity fosters the belief that the mechanism of the formation of the initial reaction centers is the same as in the thermal decomposition of Ag_2CO_3.

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